# organic compounds

# N-[4-(Morpholinodiazenyl)phenyl]-acetamide

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The title compound, $C_{12}H_{16}N_4O_2$, is a member of a family of morpholine-substituted aromatic diazenes. Conjugation of the diazene group $\pi$-system and the lone pair of electrons of the morpholine N atom is evidenced by a lengthened N=N double bond of 1.2707 (19) Å and a shortened N—N single bond of 1.346 (2) Å. The bond angles at the morpholine N atom range from 113.52 (14) to 121.12 (14)°, indicating some degree of $sp^2$ hybridization. The morpholine ring adopts a conventional chair conformation with the diazenyl group in the equatorial position. The diazenyl and acetamido groups are both twisted relative to the plane of the benzene ring by 12.3 (2) and 25.5 (3)°, respectively.

## Related literature

The title compound was synthesized using a modification of the method of Sengupta et al. (1998). For similar structures, see: Little et al. (2008). For information about diazene derivatives, see: Chen et al. (2005); Lalezari & Afgahi (1975). For bond-length data, see: Allen et al. (1987).
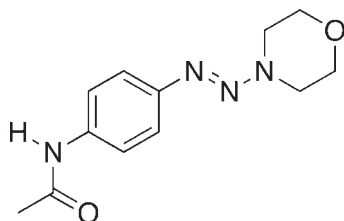


## Experimental

### Crystal data

$C_{12}H_{16}N_4O_2$
$M_r = 248.29$
Monoclinic, $P2_1/c$
$a = 12.6013$ (4) Å
$b = 10.6114$ (3) Å
$c = 9.2967$ (2) Å
$\beta = 93.874$ (2)°

$V = 1240.29$ (6) Å$^3$
$Z = 4$
Cu $K\alpha$ radiation
$\mu = 0.77$ mm$^{-1}$
$T = 90$ K
$0.23 \times 0.17 \times 0.01$ mm

### Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
$T_{min} = 0.843$, $T_{max} = 0.992$

11437 measured reflections
2249 independent reflections
1655 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.095$
$S = 1.03$
2249 reflections
168 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.20$ e Å$^{-3}$
$\Delta\rho_{min} = -0.20$ e Å$^{-3}$

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

## References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L. & Orpen, A. G. (1987). J. Chem. Soc. Perkin Trans. 2, pp. S1–19.
Bruker (2006). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, B., Flatt, A. K., Jian, H., Hudson, J. L. & Tour, J. M. (2005). Chem. Mater. 17, 4832–4836.
Farrugia, L. J. (1997). J. Appl. Cryst. 30, 565.
Lalezari, I. & Afgahi, F. (1975). J. Pharm. Sci. 64, 698–699.
Little, V. R., Jenkins, H. & Vaughan, K. (2008). J. Chem. Crystallogr. 38, 447–452.
Sengupta, S., Bhattacharyya, S. & Sadhukhan, S. K. (1998). J. Chem. Soc. Perkin Trans. 1, pp. 275–277.
Sheldrick, G. (2004). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.

# supporting information

# *N*-[4-(Morpholinodiazenyl)phenyl]acetamide

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### S1. Comment

Diazene derivatives have found utility in various research areas (Lalezari & Afgahi, 1975; Chen *et al.*, 2005). Our research uses morpholine-substituted aryl diazenes as easily handled and prepared equivalents for the *in situ* generation of diazonium ions that are then used in the synthesis of novel derivatives of *trans*–stilbene *via* a Heck-type reaction (Sengupta *et al.*, 1998).

   The structure of the title compound is shown in Figure 1. The N–N double bond adopted a *trans*-configuration. A N3–N2–N1 bond angle of 113.93 (14) ° deviates from the optimal trigonal planar geometry by approximately 6°. The diazene moiety, N3–N2–N1, exhibits $\pi$ –delocalization, evidenced by N1–N2 and N2–N3 bond lengths of 1.346 (2) and 1.2707 (19) Å respectively. These values are between literature value of 1.222 Å for a N–N double bond and 1.420 Å for a N($sp^2$)–N($sp^3$) single bond (Allen *et al.*, 1987) Morpholine nitrogen bond angles that ranged from 113.52 (14)–121.12 (14)° indicated that the morpholine nitrogen had some degree of $sp^2$ hybridization and participated in $\pi$ –delocalization. The morpholine ring adopted a conventional chair conformation,with the diazenyl group in the equitorial postion on the morpholine nitrogen, N3. The acetamino and diazene groups were found to be twisted 25.5 (3)° and 12.3 (2)° respectively from the plane of the phenyl ring. The structure of the title compound is similar to the structure of related diazenes (Little *et al.*, 2008).

### S2. Experimental

Synthetic procedures were carried out using standard techniques. Solvents and reagents were used as received. Melting points were determined in open capillaries and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a Jeol ECX 300 MHz spectrometer using TMS as the internal standard. The IR spectrum was recorded as a KBr disk on a JASCO 460 F T–IR.

   4.26 g of *N*–(4-aminophenyl)acetamide (28.4 mmol) was added to 12.5 ml of 6 *M* HCl in an ice water bath and cooled to 0° C to yield a light pink precipitate. The solid was maintained at 0° C, and a solution of 2.08 g (30.09 mmol) of NaNO₂ in 4.0 ml H₂O was added dropwise with stirring over ten minutes; a dark green brown solution resulted. After stirring for twenty minutes, 2.70 ml morpholine (2.74 g, 31.42 mmol) was added dropwise in 10 minutes. Then saturated K₂CO₃ was added until pH of 8 was reached, and solution was stirred for ten minutes: a yellow brown suspension resulted. The tan solid was collected using vacuum filtration, washed well with water and dried in air. The crude product was recrystallized from a 1:3 benzene:cyclohexane mixture to give 3.55 g (50.4%) of 4-[(*E*)-(acetamidophenyl)diazenyl]-morpholine as a tan microcrystalline solid.

   m.p. 448-449 K. IR (KBr) 3294, 3055, 2971, 1664, 1600 cm⁻¹· $^1$H NMR (300 MHz, CD₃CN): 2.03 (s, 3H), 3.67 (m, 4H), 3.77 (m, 4H), 7.33 (d, 2H), 7.51 (d, 2H), 8.33 (s, 1H). $^{13}$C NMR (75 MHz, DMSO–d*6*): 24.54, 48.33, 66.05, 119.89, 121.27, 138.28, 145.50, 168.75 p.p.m.. $R_f$ = 0.61 (ethyl acetate)

## S3. Refinement

H atoms on C were placed in idealized positions with C—H distances 0.95 - 0.99 Å and thereafter treated as riding. A torsional parameter was refined for the methyl group. The N—H hydrogen atom was placed from a difference map, and its coordinates were refined. $U_{iso}$ for H were assigned as 1.2 times $U_{eq}$ of the attached atoms (1.5 for methyl).
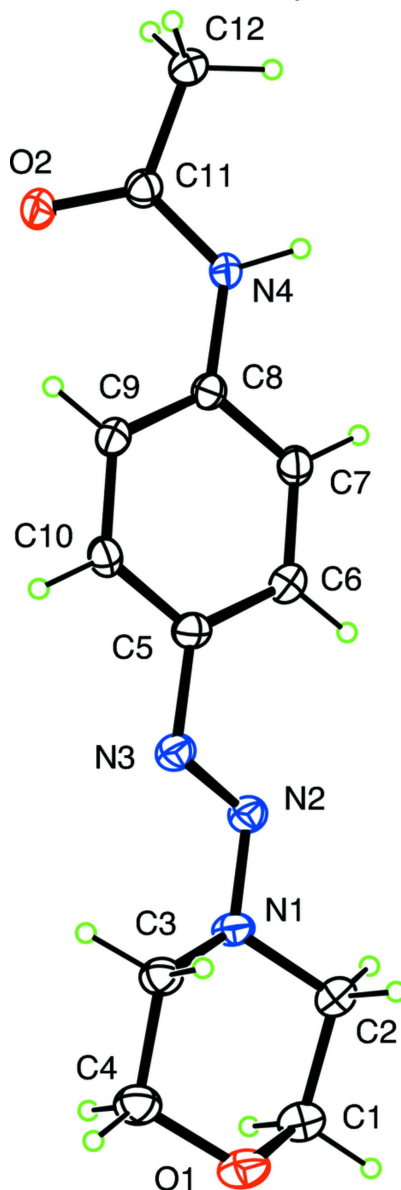


**Figure 1**

Molecular structure of the title compound with displacement ellipsoids at the 50% probability level. H atoms are shown with arbitrary radius.

### *N*-[4-(Morpholinodiazenyl)phenyl]acetamide

*Crystal data*

| | |
|---|---|
| $C_{12}H_{16}N_4O_2$ | Monoclinic, $P2_1/c$ |
| $M_r = 248.29$ | Hall symbol: -P 2ybc |

$a = 12.6013 (4)$ Å

$b = 10.6114 (3)$ Å

$c = 9.2967 (2)$ Å

$\beta = 93.874 (2)°$

$V = 1240.29 (6)$ Å$^3$

$Z = 4$

$F(000) = 528$

$D_x = 1.330$ Mg m$^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 1544 reflections

$\theta = 3.5–67.6°$

$\mu = 0.77$ mm$^{-1}$

$T = 90$ K

Plate, colorless

$0.23 \times 0.17 \times 0.01$ mm

*Data collection*

Bruker Kappa APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and $\omega$ scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)

$T_{min} = 0.843$, $T_{max} = 0.992$

11437 measured reflections

2249 independent reflections

1655 reflections with $I > 2\sigma(I)$

$R_{int} = 0.053$

$\theta_{max} = 68.8°$, $\theta_{min} = 3.5°$

$h = -15 \rightarrow 14$

$k = -12 \rightarrow 12$

$l = -7 \rightarrow 11$

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.095$

$S = 1.03$

2249 reflections

168 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.3P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.20$ e Å$^{-3}$

$\Delta\rho_{min} = -0.20$ e Å$^{-3}$

Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$

Extinction coefficient: 0.0012 (2)

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.58539 (10) | 0.71775 (12) | 0.68342 (13) | 0.0281 (3) |
| O2 | 0.91392 (10) | −0.19398 (12) | 0.26306 (12) | 0.0260 (3) |
| N1 | 0.63437 (11) | 0.46590 (13) | 0.62337 (14) | 0.0203 (3) |
| N2 | 0.66849 (11) | 0.34581 (13) | 0.61964 (14) | 0.0198 (3) |
| N3 | 0.73809 (11) | 0.32649 (13) | 0.52939 (14) | 0.0204 (3) |
| N4 | 0.88774 (11) | −0.17257 (13) | 0.50181 (15) | 0.0179 (3) |
| H4N | 0.8936 (14) | −0.2115 (18) | 0.5884 (18) | 0.021* |

| | | | | |
|---|---|---|---|---|
| C1 | 0.52108 (14) | 0.61813 (17) | 0.73287 (19) | 0.0249 (4) |
| H1A | 0.4609 | 0.6025 | 0.6610 | 0.030* |
| H1B | 0.4914 | 0.6434 | 0.8244 | 0.030* |
| C2 | 0.58485 (14) | 0.49823 (17) | 0.75637 (18) | 0.0224 (4) |
| H2A | 0.6404 | 0.5104 | 0.8357 | 0.027* |
| H2B | 0.5376 | 0.4289 | 0.7836 | 0.027* |
| C3 | 0.69258 (14) | 0.56752 (16) | 0.55717 (18) | 0.0218 (4) |
| H3A | 0.7116 | 0.5419 | 0.4598 | 0.026* |
| H3B | 0.7591 | 0.5859 | 0.6163 | 0.026* |
| C4 | 0.62278 (15) | 0.68384 (17) | 0.54677 (19) | 0.0258 (4) |
| H4A | 0.6637 | 0.7550 | 0.5095 | 0.031* |
| H4B | 0.5611 | 0.6679 | 0.4775 | 0.031* |
| C5 | 0.77020 (13) | 0.19715 (16) | 0.52560 (17) | 0.0181 (4) |
| C6 | 0.74615 (13) | 0.10620 (16) | 0.62701 (17) | 0.0199 (4) |
| H6 | 0.7041 | 0.1279 | 0.7044 | 0.024* |
| C7 | 0.78367 (13) | −0.01525 (16) | 0.61454 (17) | 0.0192 (4) |
| H7 | 0.7660 | −0.0773 | 0.6826 | 0.023* |
| C8 | 0.84737 (13) | −0.04798 (16) | 0.50304 (16) | 0.0169 (4) |
| C9 | 0.87227 (14) | 0.04281 (16) | 0.40320 (17) | 0.0188 (4) |
| H9 | 0.9155 | 0.0216 | 0.3270 | 0.023* |
| C10 | 0.83377 (13) | 0.16458 (16) | 0.41515 (17) | 0.0186 (4) |
| H10 | 0.8512 | 0.2265 | 0.3468 | 0.022* |
| C11 | 0.92053 (13) | −0.23624 (16) | 0.38778 (17) | 0.0189 (4) |
| C12 | 0.96655 (14) | −0.36422 (16) | 0.42131 (18) | 0.0217 (4) |
| H12A | 0.9306 | −0.4270 | 0.3579 | 0.033* |
| H12B | 0.9564 | −0.3855 | 0.5220 | 0.033* |
| H12C | 1.0427 | −0.3637 | 0.4058 | 0.033* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0306 (7) | 0.0194 (7) | 0.0348 (7) | −0.0004 (6) | 0.0055 (6) | −0.0053 (6) |
| O2 | 0.0442 (8) | 0.0191 (7) | 0.0147 (6) | 0.0039 (6) | 0.0025 (5) | −0.0009 (5) |
| N1 | 0.0226 (7) | 0.0150 (7) | 0.0236 (7) | 0.0021 (6) | 0.0038 (6) | −0.0025 (6) |
| N2 | 0.0215 (7) | 0.0184 (8) | 0.0195 (7) | 0.0007 (6) | 0.0002 (6) | −0.0021 (6) |
| N3 | 0.0221 (7) | 0.0192 (8) | 0.0199 (7) | 0.0012 (6) | 0.0009 (6) | −0.0028 (6) |
| N4 | 0.0243 (8) | 0.0160 (7) | 0.0136 (7) | 0.0016 (6) | 0.0025 (6) | 0.0012 (6) |
| C1 | 0.0229 (9) | 0.0227 (10) | 0.0293 (9) | 0.0014 (8) | 0.0027 (8) | −0.0037 (8) |
| C2 | 0.0232 (9) | 0.0229 (10) | 0.0215 (9) | 0.0006 (7) | 0.0040 (7) | −0.0033 (8) |
| C3 | 0.0244 (9) | 0.0168 (9) | 0.0247 (9) | −0.0009 (8) | 0.0042 (8) | −0.0008 (7) |
| C4 | 0.0296 (10) | 0.0185 (9) | 0.0294 (10) | −0.0005 (8) | 0.0023 (8) | −0.0016 (8) |
| C5 | 0.0173 (8) | 0.0173 (9) | 0.0190 (8) | 0.0002 (7) | −0.0025 (7) | −0.0032 (7) |
| C6 | 0.0197 (9) | 0.0225 (10) | 0.0179 (8) | −0.0005 (7) | 0.0029 (7) | −0.0027 (7) |
| C7 | 0.0218 (9) | 0.0198 (9) | 0.0162 (8) | −0.0010 (7) | 0.0016 (7) | 0.0010 (7) |
| C8 | 0.0185 (8) | 0.0169 (9) | 0.0148 (8) | −0.0001 (7) | −0.0018 (7) | −0.0022 (7) |
| C9 | 0.0214 (8) | 0.0198 (9) | 0.0152 (8) | 0.0001 (7) | 0.0018 (7) | −0.0013 (7) |
| C10 | 0.0220 (8) | 0.0180 (9) | 0.0157 (8) | −0.0021 (7) | 0.0001 (7) | 0.0023 (7) |
| C11 | 0.0207 (9) | 0.0180 (9) | 0.0179 (9) | −0.0009 (7) | 0.0010 (7) | −0.0009 (7) |

| C12 | 0.0277 (9) | 0.0182 (9) | 0.0194 (8) | 0.0023 (8) | 0.0030 (7) | −0.0020 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.427 (2) | C3—H3B | 0.9900 |
| O1—C4 | 1.430 (2) | C4—H4A | 0.9900 |
| O2—C11 | 1.2407 (19) | C4—H4B | 0.9900 |
| N1—N2 | 1.346 (2) | C5—C10 | 1.388 (2) |
| N1—C2 | 1.463 (2) | C5—C6 | 1.397 (2) |
| N1—C3 | 1.463 (2) | C6—C7 | 1.380 (2) |
| N2—N3 | 1.2707 (19) | C6—H6 | 0.9500 |
| N3—C5 | 1.432 (2) | C7—C8 | 1.397 (2) |
| N4—C11 | 1.345 (2) | C7—H7 | 0.9500 |
| N4—C8 | 1.417 (2) | C8—C9 | 1.388 (2) |
| N4—H4N | 0.903 (17) | C9—C10 | 1.387 (2) |
| C1—C2 | 1.513 (2) | C9—H9 | 0.9500 |
| C1—H1A | 0.9900 | C10—H10 | 0.9500 |
| C1—H1B | 0.9900 | C11—C12 | 1.501 (2) |
| C2—H2A | 0.9900 | C12—H12A | 0.9800 |
| C2—H2B | 0.9900 | C12—H12B | 0.9800 |
| C3—C4 | 1.515 (2) | C12—H12C | 0.9800 |
| C3—H3A | 0.9900 | | |
| | | | |
| C1—O1—C4 | 109.15 (13) | O1—C4—H4B | 109.2 |
| N2—N1—C2 | 113.52 (14) | C3—C4—H4B | 109.2 |
| N2—N1—C3 | 121.12 (14) | H4A—C4—H4B | 107.9 |
| C2—N1—C3 | 115.93 (14) | C10—C5—C6 | 119.32 (16) |
| N3—N2—N1 | 113.93 (14) | C10—C5—N3 | 115.78 (15) |
| N2—N3—C5 | 112.31 (14) | C6—C5—N3 | 124.83 (14) |
| C11—N4—C8 | 127.19 (14) | C7—C6—C5 | 119.82 (15) |
| C11—N4—H4N | 117.5 (12) | C7—C6—H6 | 120.1 |
| C8—N4—H4N | 115.3 (12) | C5—C6—H6 | 120.1 |
| O1—C1—C2 | 111.22 (14) | C6—C7—C8 | 120.77 (16) |
| O1—C1—H1A | 109.4 | C6—C7—H7 | 119.6 |
| C2—C1—H1A | 109.4 | C8—C7—H7 | 119.6 |
| O1—C1—H1B | 109.4 | C9—C8—C7 | 119.38 (16) |
| C2—C1—H1B | 109.4 | C9—C8—N4 | 123.00 (15) |
| H1A—C1—H1B | 108.0 | C7—C8—N4 | 117.55 (14) |
| N1—C2—C1 | 109.14 (14) | C10—C9—C8 | 119.79 (15) |
| N1—C2—H2A | 109.9 | C10—C9—H9 | 120.1 |
| C1—C2—H2A | 109.9 | C8—C9—H9 | 120.1 |
| N1—C2—H2B | 109.9 | C9—C10—C5 | 120.90 (16) |
| C1—C2—H2B | 109.9 | C9—C10—H10 | 119.5 |
| H2A—C2—H2B | 108.3 | C5—C10—H10 | 119.5 |
| N1—C3—C4 | 108.78 (14) | O2—C11—N4 | 123.37 (15) |
| N1—C3—H3A | 109.9 | O2—C11—C12 | 121.44 (15) |
| C4—C3—H3A | 109.9 | N4—C11—C12 | 115.19 (14) |
| N1—C3—H3B | 109.9 | C11—C12—H12A | 109.5 |

| | | | | |
|---|---|---|---|---|
| C4—C3—H3B | 109.9 | C11—C12—H12B | 109.5 | |
| H3A—C3—H3B | 108.3 | H12A—C12—H12B | 109.5 | |
| O1—C4—C3 | 111.89 (14) | C11—C12—H12C | 109.5 | |
| O1—C4—H4A | 109.2 | H12A—C12—H12C | 109.5 | |
| C3—C4—H4A | 109.2 | H12B—C12—H12C | 109.5 | |
| | | | | |
| C2—N1—N2—N3 | −159.87 (14) | N3—C5—C6—C7 | −178.36 (16) | |
| C3—N1—N2—N3 | −14.8 (2) | C5—C6—C7—C8 | 1.3 (3) | |
| N1—N2—N3—C5 | −178.35 (13) | C6—C7—C8—C9 | −0.5 (2) | |
| C4—O1—C1—C2 | 62.57 (18) | C6—C7—C8—N4 | 176.59 (16) | |
| N2—N1—C2—C1 | −163.16 (14) | C11—N4—C8—C9 | −25.5 (3) | |
| C3—N1—C2—C1 | 49.87 (19) | C11—N4—C8—C7 | 157.45 (16) | |
| O1—C1—C2—N1 | −55.31 (19) | C7—C8—C9—C10 | 0.0 (2) | |
| N2—N1—C3—C4 | 166.58 (14) | N4—C8—C9—C10 | −176.97 (16) | |
| C2—N1—C3—C4 | −49.15 (19) | C8—C9—C10—C5 | −0.2 (3) | |
| C1—O1—C4—C3 | −62.36 (19) | C6—C5—C10—C9 | 0.9 (2) | |
| N1—C3—C4—O1 | 54.28 (19) | N3—C5—C10—C9 | 178.10 (15) | |
| N2—N3—C5—C10 | 170.70 (14) | C8—N4—C11—O2 | −4.0 (3) | |
| N2—N3—C5—C6 | −12.3 (2) | C8—N4—C11—C12 | 175.96 (16) | |
| C10—C5—C6—C7 | −1.4 (2) | | | |

### Hydrogen-bond geometry (Å, º)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N4—H4N···O2[i] | 0.903 (17) | 1.911 (18) | 2.8115 (18) | 174.5 (17) |

Symmetry code: (i) *x*, −*y*−1/2, *z*+1/2.